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INVESTIGATION OF LITHIATED CARBONS BY TRANSMISSION ELECTRON MICROSCOPY AND X-RAY DIFFRACTION ANALYSIS

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ABSTRACT

The microstructures of lithiated synthetic graphite and carbon black were studied by high-resolution transmission electron microscopy (HRTEM) and X-ray diffraction (XRD) analysis. Information about the crystal structure of carbon containing various Li compositions can provide useful insights to our understanding of the Li storage mechanism in carbonaceous materials. Samples with compositions of $\text{Li}_{0.93}\text{C}_6$ or $\text{Li}_{0.45}\text{C}_6$ were found to contain both stage-one and stage-two compounds. These observations are consistent with XRD data. The changes in sample microstructure as the results of lithiation and exposure to electron irradiation were observed by TEM and recorded over several minutes in the microscope environment. Selected area electron diffraction patterns indicated that the lithiated samples quickly changed composition to LiC_{24} , which appeared to dominate during the brief analysis period. The layer planes in the lattice image of a disordered carbon black after Li insertion are poorly defined, and changes in the microstructure of these lithiated carbons was not readily apparent. Observations on these lithium intercalation compounds as well as the limitation of the experimental procedure will be presented.

INTRODUCTION

Lithiated carbons are used in the negative electrode in Li-ion cells. The most suitable type of carbon and the mechanism by which Li is stored in the carbon structure are subjects of intense discussion in the literature (1-5). Among the techniques used to study the structure of lithium intercalated carbons, only transmission electron microscopy (TEM) can provide direct imaging of the materials at the microstructural level. These informations would provide valuable insights into the lithium intercalation processes.

The use of TEM to investigate graphite intercalation compounds (GICs) has been conducted (6-13). Millward and Jefferson (6) presented a review on TEM of carbons, including intercalated graphite compounds containing potassium or FeCl_3 . Thomas and co-workers examined the structure of potassium (7) and FeCl_3 (8) intercalated in natural graphite by TEM. The micrographs clearly showed evidence for a lattice image that is attributed to the distinct layers of intercalant and graphite. In a subsequent paper, Thomas and co-workers (9) reported the direct observation of interpenetrating stages of FeCl_3 in graphite. Kambe et al. (10) reported that Li and other alkali metals (Rb, Cs, K) intercalated and formed island structures between the graphite layer planes. These islands were observed by bright-field and dark-field TEM. Dresselhaus and co-workers (10-13) conducted extensive studies of alkali metals intercalated in highly oriented pyrolytic graphite (HOPG). The size of the electron beam ($\sim 1 \mu\text{m}$ or less) is comparable in size to that of the crystallites in HOPG, making detailed structural analysis more meaningful. The electron diffraction beam was oriented in the c-axis direction of thin specimens (about 500 \AA) of the intercalated HOPG where diffraction patterns with well-defined diffraction spots are observed.

TEM studies involving lithium intercalation carbons are limited (5, 13-15). Dresselhuus and co-workers have reported the lattice image of single-crystal HOPG containing lithium species (13). Sato et al. (5) used high-resolution TEM to examine the difference in microstructure of disordered carbon containing lithium (carbonized polyphenylene) and the pristine material. The interlayer spacing is reported to increase by about 10% to ~ 4 Å after Li insertion in the disordered carbon, comparable to the percentage change reported for Li intercalation in graphite. The storage of lithium in these disordered carbons was thought to create a more defective microstructure.

This paper presents the TEM and XRD results obtained on the microstructure of graphite and carbon blacks that contained intercalated lithium. The morphology and microstructure of these materials are characteristic of a wide range of high-capacity carbons for Li-ion cells. These observations are expected to provide additional information on lithiated carbons to complement the information obtained by other techniques such as X-ray diffraction (XRD) analysis, Raman spectroscopy and scanning tunneling microscopy (STM), and to extend our understanding of the Li storage mechanism in carbonaceous materials. In addition, TEM provides information on microstructural changes, both relevant to processes occurring on the surface and in the bulk of the carbonaceous materials. The effect of the electron beam on the TEM image is discussed. The results of this study will be helpful in our efforts to fabricate an *in situ* electrochemical cell for TEM observations, which was started (15) but was not successful because of problems with processing of the cell components.

EXPERIMENTAL

Synthetic graphite and carbon black represent the two types of microstructures characteristic of materials that have high reversible lithium intercalation capacity. The lithiated graphite and carbon samples were prepared by electrochemical lithiation method. Fully intercalated carbons were also prepared by chemical means via a direct contact between a lithium metal foil and the carbon sample in the electrolyte. Details on both techniques were reported (14). Electrodes containing synthetic graphite (SFG6, Timcal AG, Sins, Switzerland) or carbon black (Sterling R, Cabot Corp., Billerica, MA, USA) were prepared by mixing with a PYDF binder and pressed onto a copper-foil current collector. The electrolyte was 50/50 ethylene carbonate (EC)/dimethylcarbonate (DMC) (Grant Chemical) containing 0.5M Lithium trifluoromethanesulfonimide, $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ (HQ115, 3M Corp.). These samples were intercalated/deintercalated electrochemically at a C/24 rate using a procedure described elsewhere (16). Samples with a final composition of close to LiC_6 or LiC_{12} were obtained by terminating the deintercalation process at a predetermined time during the second cycle. The lithium loaded electrodes were washed in a fresh (50:50) EC/DMC solvent for about fifteen minutes after the lithiation experiments, soaked quickly several times in DMC solvent, then dried under vacuum.

For TEM analysis, the sample was ground into a fine powder, and dispersed onto a holey carbon film. For XRD analysis, the lithiated carbon was sealed in 2 cm-ampoules made from shrinkable polyethylene tubing sealed on both ends. The encapsulated sample was examined directly in the X-ray diffractometer. All sample preparation was conducted inside a glove box (<15 ppm H_2O) to avoid possible contamination by water, oxygen or other impurities that can react with lithium. The samples were then stored in argon-filled vials that was sealed with wax (Parawax, Bromar, Inc.) for transport. Lithiated carbon samples stored in this fashion were found to be stable for several days in ambient conditions.

The HRTEM facilities available at the National Center for Electron Microscopy at Lawrence Berkeley National Laboratory were utilized in this study. TEM analysis at high resolution was done using a Topcon-002B operated at 200 kV and a filament current of about 10 μA . Conventional techniques were applied in the TEM studies of the samples. The instrument was adjusted to optimize the images where needed. No systematic study involving the defocus of

the objective lens was conducted. The XRD analyses were performed using a diffractometer (Siemens Diffractometer OSP, Model:D500, Germany)

MICROSTRUCTURE OF LITHIATED GRAPHITE

Several samples of the lithium intercalated graphite with compositions about $\text{Li}_{0.93}\text{C}_6$ and $\text{Li}_{0.45}\text{C}_6$ were examined by TEM and XRD. The final compositions in these samples were determined coulombically from the intercalation process during the second cycle after subtracting any amount associated with the lithium allowed to deintercalate. Figure 1 shows typical performance of the synthetic graphite and the carbon black. The arrows indicate the time at which the experiments were terminated for sample recovery. While both types of materials represent the different degree of order in the carbon structure, they have comparable reversible capacity for lithium intercalation.

The TEM samples are briefly exposed to air (< 1 minute) when they are removed from the sealed vials and inserted into the electron microscope chamber. Small specimens of fully lithiated graphite has been found to be stable during several minutes exposure to air as suggested by the retention of the characteristic golden color associated with lithiated graphite. Kinno et al. (17) observed similar stability in their STM studies of a stage-one lithiated graphite that was exposed briefly to air. Therefore, the introduction of the specimen from the sealed transport vial into the instrument chamber was not expected to affect the lithiated structure to a significant extent. The presence of lithium in the graphite sample in the TEM analysis was confirmed by examining the sample under the Electron Energy Loss Spectroscopy (EELS) mode. The presence of a peak centered around 60 eV suggests lithium was present. In addition, XRD analysis of the encapsulated samples prepared from the same electrode showed peaks associated with staged-one and -two compounds, further confirming the presence of lithium. Both EELS and XRD were useful for confirming the presence of lithium in samples where visual observation was limited (i.e., stage-two graphites and lithiated carbon blacks).

TEM analysis provides clear images of the changes in the microstructure of lithiated graphite relative to that of pristine materials. We have reported the lattice image of highly ordered synthetic graphite, SFG6, where d_{002} spacing of 3.35 Å was observed (14). Fig. 2 shows an image of a lithiated sample ($\text{Li}_{0.93}\text{C}_6$) with lattice fringes corresponding to LiC_6 and LiC_{12} . A d -spacing of about 3.56 Å is measured in domain A (see Fig. 2), which is commensurate with $d_{002} = 3.53$ Å in LiC_{12} . These lattice fringes are observed over large areas indicating that LiC_{12} is the dominant phase in this domain of the particle. Other domain (labeled B in the figure) show lattice fringes of 2.62 Å, which are attributed to the (101) planes of LiC_6 . The micrograph shows lengthy areas of dark contrast that appear to be nearly parallel to each other. These areas can be associated with domains of different compositions (intercalation stages). The results here and our experience indicate that there are several staged compounds that appear to be randomly distributed throughout the examined sample regardless of the overall composition.

The presence of a mixture of multiple intercalating stages has been reported by several workers (18-21). The above TEM observations suggest that regions of different lithium concentration are present in the particles of lithiated graphite. Lag et al. (19) observed island-like structures (500-2000 Å) in stage-one lithiated graphite by STM, which they attribute to inhomogeneities in the spatial distribution of lithium. Mittleman (20) used an analytical scanning TEM to investigate the in-plane structure of Rb-intercalated graphite, and he concluded that the island-like structure that was observed is due to the nucleation of Rb in the Dumas-Herold domains which are typically about 2000 Å across. The island domains in our lithiated graphite samples are expected to be much smaller because the crystallite size is less than 1000 Å.

As evident in Figure 2 and other images reported in this paper, the lattice images and the diffraction patterns are more complex than those observed from a single crystalline material such as HOPG. The polycrystalline nature of the synthetic graphite (SFG6) used in this study resulted in the presence of randomly oriented crystallites. In addition, the variation in the microstructure

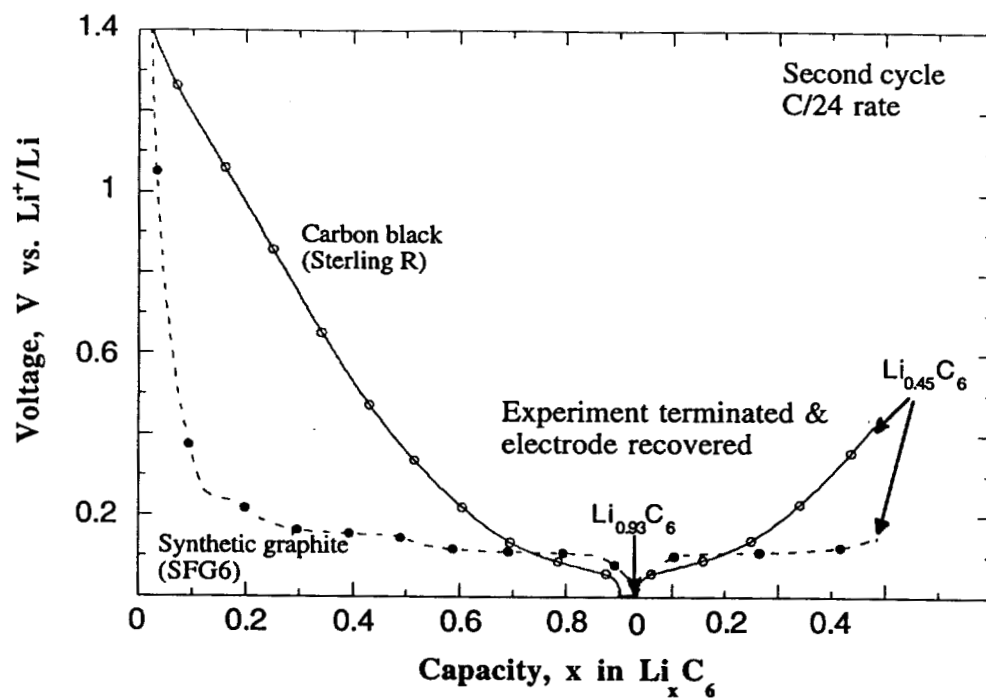


Fig. 1. Electrochemical intercalation profile of the synthetic graphite and carbon black. Arrows indicate termination points for sample recovery.

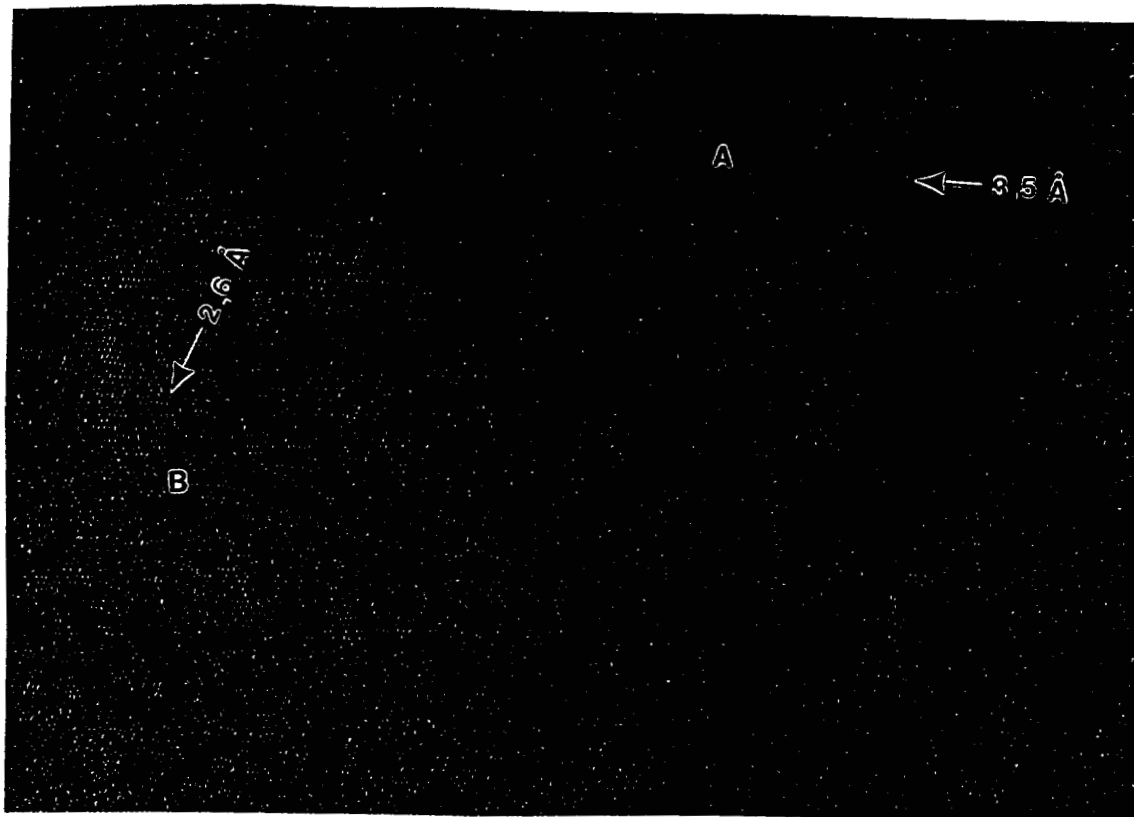


Fig. 2. Lattice image of a lithiated SFG6 graphite particle with $\text{Li}_{0.93}\text{C}_6$ composition.

expected from intercalated lithium compounds, the crystallite size and the sample thickness all contribute to the image resolution, the diffraction pattern resolution and spot intensities.

Our XRD analyses showed a mixture of stage-one and stage-two phases for most samples. The ratio of these peaks, however, varies and qualitatively depends on the overall composition of the samples. Uchida and Tomura (22) showed by *in-situ* XRD clear evidence for the formation of different staging compounds during Li intercalation/de-intercalation of graphite. With the stage-one compound ($x = 1$ in Li_xC_6), only a single major diffraction peak at $2\theta = 24^\circ$ is observed. When x decreases, the peak at $2\theta = 24^\circ$ decreases and a peak at $2\theta = 25.2^\circ$ corresponding to the stage-two compound emerges. As x decreases further, an additional peak at $2\theta = 26.6^\circ$ for the stage-three compound becomes evident. Roh et al. (18) conducted *in-situ* XRD studies of lithiated graphite and identified diffraction peaks for the stage-two, -three and -four compounds at slightly different 2θ from those reported by Uchida and Tomura (22).

The solid electrolyte interface (SEI) formed on the graphite surface can be expected from the lithiated graphite samples regardless of the method used for lithiation. The EELS spectra of lithiated graphite in our samples showed the K-edges of lithium, carbon and oxygen (60, 300 and 550 eV, respectively). However, we can not associate the lithium solely with the SEI layer because lithium is also present between the layer planes in the graphite. Naji et al. (23) observed the presence of a SEI layer on their natural graphite (UF4, Le Carbone Lorraine) from TEM images and the evidence of Li_2CO_3 in electron energy-loss spectroscopy (EELS) studies. They attributed the lithium to the SEI layer because the graphite sample was anodically polarized to 2 V where lithium ions would not remain in the graphite structure.

STABILITY OF LITHIATED GRAPHITE

We have previously reported on TEM observations of lithiated graphite (14,15). Detailed observation of these compounds over extended period of time was not successful due to the instability of the image. The stability of the graphite intercalation compounds in the environment of the TEM is poor. Lithiated carbons have been thought to undergo decomposition in the vacuum environment and upon electron irradiation. These issues will be examined in more detail here.

Electron irradiation induces changes in organic and inorganic materials during TEM studies, and factors such as the beam type, radiation dose, sample and temperature have an impact (24). Thomas and co-workers (8) observed, for example, that FeCl_3 in the stage-one graphite compound desorbs or decomposes in the vacuum of an electron microscope to form the residue compound. Kambe et al. (25) reported that Rb desorption occurs from the edge of Rb-intercalated graphite (HOPG) crystallites except at sample temperatures < 300 K in the electron microscope. Above 300K, the superlattice diffraction spots decrease in intensity and second-neighbor graphite spots appear to join together to form lines.

In light of these issues and our interest in *in situ* examination of the lithium intercalation process with TEM, additional experiments were conducted. The lithiated graphite samples were studied by comparing TEM images and selected area diffraction patterns over time. The SAED along the $\langle 110 \rangle$ direction in Figures 3a and 3b were taken in sequence about 30 seconds apart while the sample was irradiated by 200-keV electrons in the microscope. The markers help to illustrate the changes that occur in the lithiated graphite during the interval of electron irradiation. The diffraction spots in Fig. 3a were indexed to d spacing of 3.65 Å and 2.21 Å, approximating the compounds with the composition LiC_6 (3.70 Å and 2.15 Å). The SAED pattern in Fig. 3b was obtained about 30 s after Fig. 3a. It shows evidence for small changes in the layer separation as manifested in the reduction in the size and intensity of certain spots. Diffraction spots 1 and 4 became larger and cone-like, connecting with neighboring spots along the $\langle 001 \rangle$ direction, while the diffraction spots 2 and 3 became smaller and weaker in intensity. These changes in the SAED pattern are attributed to the loss of lithium ions and the concomitant decrease in the distance between the layer planes. The SAED pattern shows streaking of the diffraction spots, attributable to contribution from layer planes associated with randomly

distributed staged compounds. Similar streaking behavior in the diffraction pattern was reported by Evans and Thomas (7) for potassium deintercalating from the graphite structure.

The stability of the intercalated compounds documented directly by TEM imaging and indirectly by SAED mode was recorded over several experiments. Fig. 4a showed a diffraction pattern of another samples with $\text{Li}_{0.9}\text{C}_6$ composition. Fig. 4b shows the SAED obtained after an additional 10 min of electron irradiation. Several diffraction spots (i.e., marked 2, 3, 4 and 5 in Fig. 4a) associated with various stage one and stage two compounds for many crystals disappear. Diffraction spot (marked 1, $d = 3.42 \text{ \AA}$) corresponding to LiC_{24} remained and increased in intensity. The results suggest that for these polycrystalline compounds with intercalated lithium, LiC_{24} appears to be the stable phase, at least during the analysis period.

Microstructural changes to the host graphite and carbon structure under these experimental conditions is not expected to occur. We have obtained many high-resolution TEM images of this graphite sample and other carbon samples under extended exposure time and have not found any observable degradation in sample images. However, carbon samples have been reported to be reactive under long duration and higher energy electron irradiation conditions. Pedraza and Koike (26) studied the effect of electron irradiation of HOPG in a TEM using a 300-keV electron beam that was focused to a diameter of about $1.3 \text{ }\mu\text{m}$. Electron irradiation at room temperature showed clear evidence for macroscopic changes in the structure of the HOPG. For instance, after about 10 h of irradiation, elongation in the c-axis direction and contraction parallel to the basal plane were observed. Nakai et al. (27) observed that HOPG transformed from graphite to amorphous carbon by prolonged irradiation by 400-keV electrons in an electron microscope.

Interaction of the electron beam with intercalant species in GIC's has been studied. High-resolution TEM was used to examine the structure and properties of $\text{Ag } \beta\text{-Al}_2\text{O}_3$ (28). Electron-beam irradiation induced the formation of "globules" and "whiskers" of silver. The diffusion of Ag^+ ions and subsequent reduction by the electron beam is reported to be the mechanism responsible for the formation of globules and whiskers. Reduction of Li^+ ions to Li metal by electrons is a possibility in the electron microscope. We were not able to find strong evidence of microscopic islands of Li metal in our samples.

Analyses of several lattice images was undertaken to determine the most stable staged-compound that is present during the brief analysis period ($\sim 20\text{-}30$ minutes). LiC_{24} was found most frequently in several electron micrographs. Examination of lithiated graphite with nominal composition of LiC_6 ($\text{Li}_{0.93}\text{C}_6$) showed similar behavior to that of LiC_{12} ($\text{Li}_{0.45}\text{C}_6$) after prolonged electron irradiation in the electron microscope. Based on this limited number of observations, LiC_{24} appeared to be the semi-stable phase under these conditions.

MICROSTRUCTURE OF LITHIATED CARBON BLACK

TEM of the pristine carbon black sample (Sterling R) shows only a short-range order with a lattice image consisting of short basal planes that roughly follow the contours of the particle, typical of carbon black particles. The high-resolution images of a pristine and intercalated sample $\text{Li}_{0.9}\text{C}_6$ are shown in Figures 5a and 5b, respectively. Qualitatively, only a small change in the microstructure takes place as the layer planes in the lattice image appear to be more poorly defined. This is in qualitative agreement with the conclusion by Sato et al. (5) who suggested that insertion of Li in a disordered carbon creates a more defective lattice. Based on the observations presented here, it is difficult to obtain clear information by TEM on the change in the microstructure of disordered carbon upon lithiation. It appears that the microstructures of the disordered carbon and the lithiated carbon are very similar.

The presence of any stage compound or changes in the microstructure was not observed in our XRD analysis of the lithiated carbon black. Tanaike and Inagaki (29) observed only broad

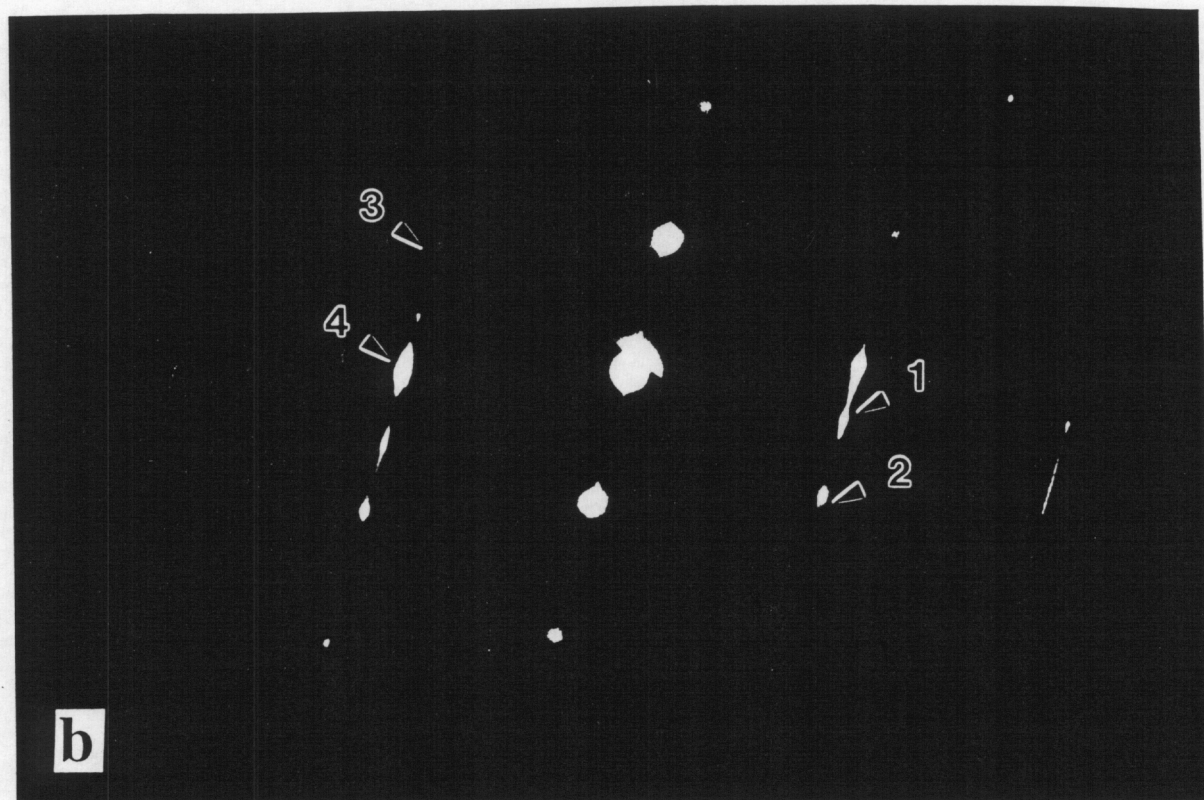
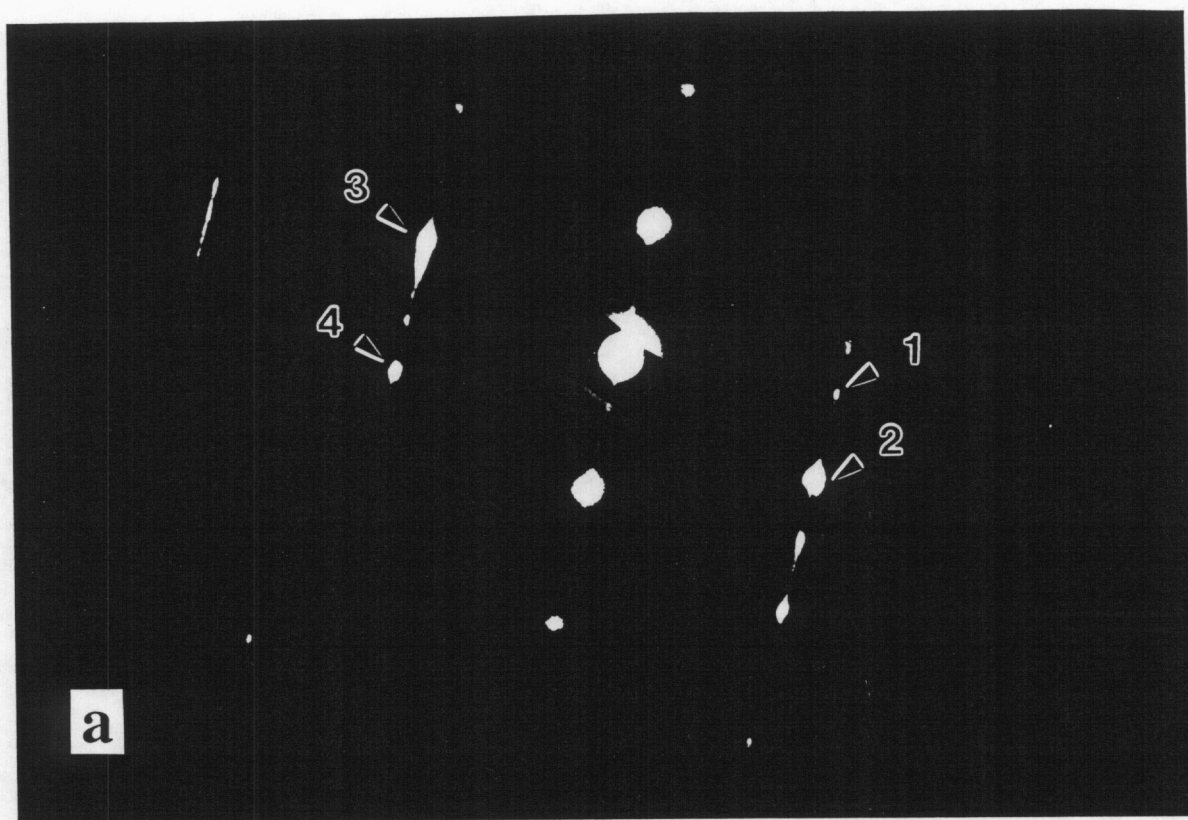


Fig. 3. Selected-area electron-diffraction pattern of $\text{Li}_{0.9}\text{C}_6$ taken after continuous exposure to electron irradiation. (a) initial; (b) taken after about 30 sec.

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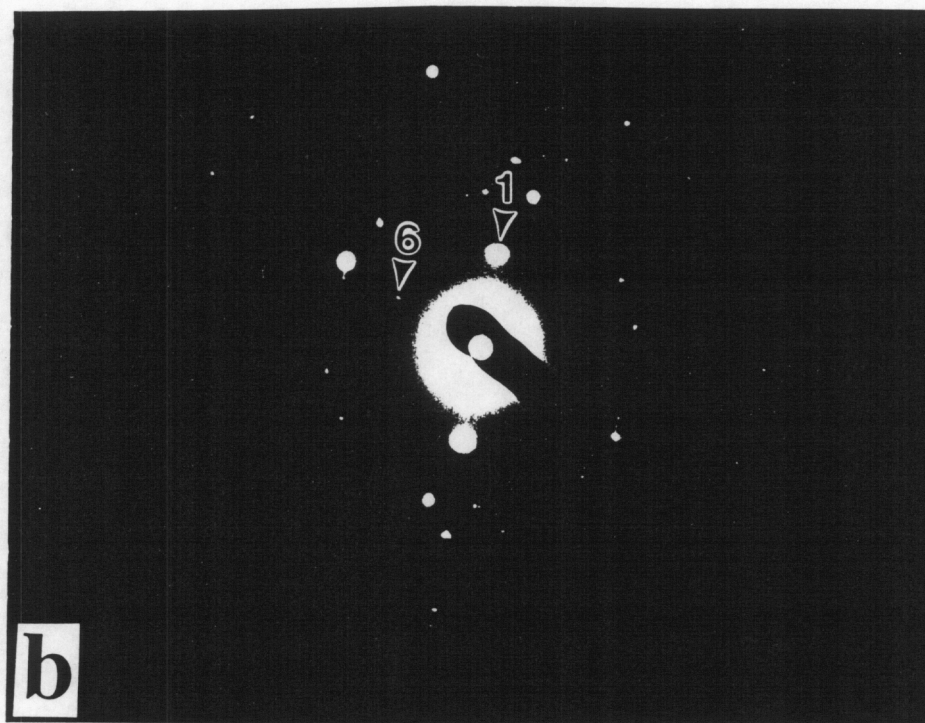
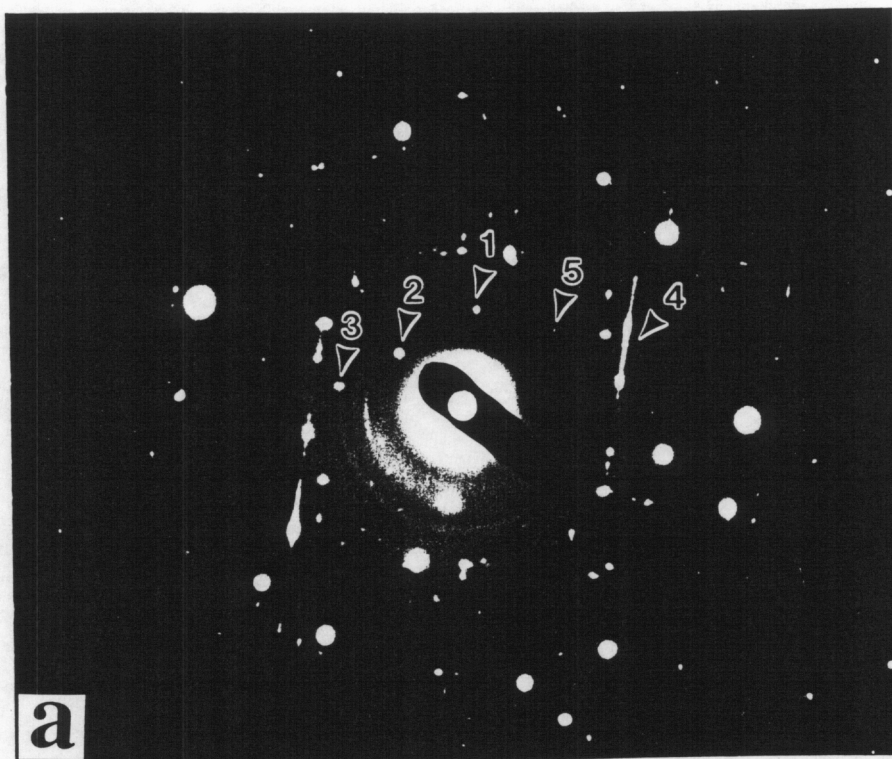


Fig. 4. Selected-area electron-diffraction pattern of a $\text{Li}_{0.9}\text{C}_6$ sample taken after continuous exposure to electron irradiation. (a) Initial, (b) after about 10 min

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XRD diffraction peaks with no strong evidence for any stage structure in their analysis of disordered carbons (i.e., low degree of graphitization, d_{002} spacing = 3.467 Å), which were prepared chemically. *In-situ* XRD studies of Li intercalation of a disordered carbon (petroleum coke) by Uchida and Tomura (22) showed that diffraction peaks indicative of staging were not conclusive.

CONCLUDING REMARKS

While transmission electron microscopy is a useful tool for investigating the microstructure of lithiated carbon, it is evident that the lithium in lithiated carbon is facile in the environment of the transmission electron microscope and is rapidly removed from the carbon microstructure. The time of exposure necessary to capture the morphology of the lithiated carbon is apparently limited to several minutes. The results suggest that *in-situ* studies of Li intercalation/de-intercalation by TEM at high resolution (i.e., accelerating voltage of 200 kV) is not possible due to rapid interaction of lithiated species with the electron beam.

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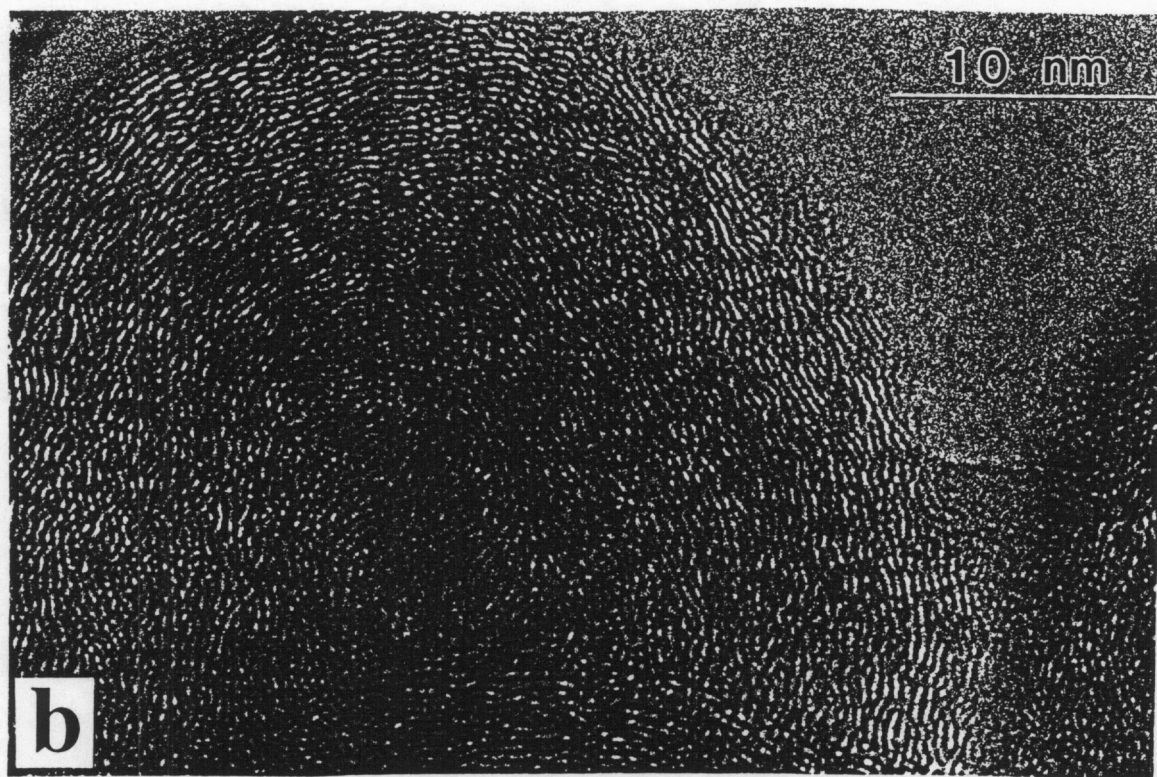
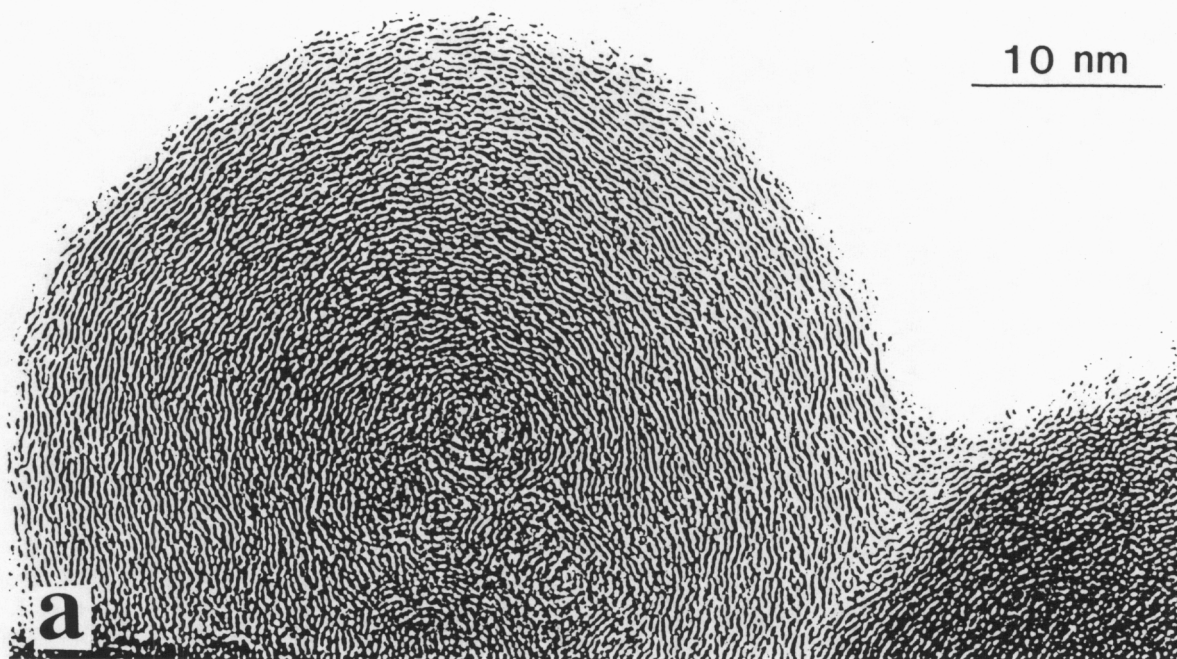


Fig. 5. Lattice image of Sterling R (thermal black) (a) pristine sample before lithiation; (b) sample with $\text{Li}_{0.9}\text{C}_6$ composition.

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